Characteristics and anticoagulation behavior of polyethylene terephthalate modified by C₂H₂ plasma immersion ion implantation-deposition

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Acetylene (C₂H₂) plasma immersion ion implantation-deposition (PIII-D) is conducted on polyethylene terephthalate (PET) to improve its blood compatibility. The structural and physicochemical properties of the modified surface are characterized by, Raman spectroscopy, x-ray photoelectron spectroscopy (XPS), and static contact angle measurement. Atomic force microscopy discloses that the average roughness (Rₐ) of film surface decreases from 58.9 nm to 11.4 nm after C₂H₂ PIII-D treats PET. Attenuated total reflection Fourier transform infrared spectroscopy shows that the specific adsorption peaks for PET decrease after ion implantation and deposition. Raman spectroscopy indicates that a thin amorphous polymer-like carbon (PLC) film is formed in the PET. The effects of the surface modification on the chemical bonding of C, H, and O are examined by XPS and the results show that the ratio of sp³ C—C to sp² C=C is 0.25. After C₂H₂ PIII-D, the polar component γ_p of surface energy increases from 2.4 mN/m to 12.3 mN/m and γ_p/γ_d increases from 0.06 to 0.35. The wettability of the modified surfaces is improved. Scanning electron microscopy and optical microscopy reveal that the amounts of adhered, aggregated and morphologically changed platelets are reduced by the deposition of an amorphous polymer-like carbon film. The thrombin time, prothrombin time, and activated partial thromboplastin time of the modified PET are longer than those of the untreated PET. Our result thus shows that the amorphous PLC film deposited on the PET surface by C₂H₂ PIII-D improves platelet adhesion and activation. © 2004 American Vacuum Society. [DOI: 10.1116/1.1633569]

I. INTRODUCTION

Poly(ethylene terephthalate) (PET) is one of the most important polymeric materials used in the biomedical field because of its excellent mechanical properties and moderate biocompatibility. In particular, it is widely adopted in cardiovascular implants, such as artificial heart valve sewing rings ¹⁻² and artificial blood vessels. ³⁻⁵ However, the blood compatibility of PET is insufficient for the long-term anti-thrombogenic demand for in vivo applications and attempts must be made to improve its blood compatibility.

Surface modification techniques, such as low-temperature plasma treatment ⁶⁻⁸ or ion implantation ⁹⁻¹¹ have been attempted to improve the blood compatibility of polymers. Plasma immersion ion implantation-deposition (PIII-D), an effective approach for the surface modification of materials, incorporates both ion implantation and low-temperature plasma processing. This burgeoning technique has been applied to polymers to improve the mechanical properties, ¹² electrical conductivity, ¹³ and gas barrier properties. ¹⁴⁻¹⁶ However, relatively little work has been reported on the surface modification of polymers by PIII-D to enhance the blood compatibility properties.

In this article, we report our study on the surface modification of PET by acetylene (C₂H₂) PIII-D. The surface structure and properties of the modified PET are characterized using laser Raman spectroscopy, attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), x-ray photoelectron spectroscopy (XPS), and contact angle measurements. The blood compatibility in vitro is evaluated by platelet adhesion observation employing optical micros-
copy and scanning electron microscopy (SEM) as well as coagulation factor experiments.

II. EXPERIMENT

A. Plasma immersion ion implantation-D treatment

The 10 μm thick PET films purchased from 3M (USA) were washed ultrasonically in methanol, acetone, and doubly distilled water for 10 min and dried in a purified biological lab. The PET films were put on a stainless substrate attached to an insulated stainless-steel electrode in the center of the vacuum chamber as shown in Fig. 1. A negative voltage was then applied to the electrode. For some samples, the carbon layer was deposited on Si (100) wafers. These wafers were placed on the PET film laid on the stainless substrate to make the same electric contact as the PET specimen.

C₂H₂ PIII was performed at a sample voltage of 5 kV for 40 min. The base pressure in the vacuum chamber was 2.4 × 10⁻³ Pa. The pressure in the vacuum chamber rose to 1.0 × 10⁻¹ Pa followed by the introduction of C₂H₂ at a flow rate of 30 standard cubic centimeters per minute. The sample
high voltage pulse width was 20 μs and frequency was 100 Hz. These samples are designated as PIII-PET in this work.

B. Surface characterization

Static contact angles were measured using the sessile drop method with a contact angle geniometer (JY-82, China) at ambient humidity and temperature. All liquid drop contact angles reported here are the mean values of six measurements on different parts of the film. ATR-FTIR spectra were acquired using a Perkin–Elmer 16PC spectrometer (20 cumulative scans) with an ATR attachment composed of a KRS-5 crystal prism at an incident angle of 45°. XPS measurements were performed using the PHI-5802 equipped with a monochromatic Al Kα source. To investigate the induced surface chemical changes, the C 1s and O 1s core-level spectra were recorded. Raman spectra were obtained by a Raman spectrometer (JobinYi, T64000) using the 514.5 nm resonant line of an Ar⁺ laser. Atomic force microscopy (AFM) studies were carried out on a Autoprobe Research System (Park Scientific Instrument) in the noncontact mode employing the PSI Image Processing and Data Analysis software.

C. In vitro platelet adhesion experiment

The samples were immersed into human fresh platelet-rich plasma (PRP) and incubated at 37 °C for 20 and 120 min. After rinsing, fixing, and critical point drying, the specimens were coated with gold palladium and examined using SEM and optical microscopy. Six fields were chosen at random to obtain averages of the quantity of the adherent platelets.
D. In vitro coagulation time tests

The antithrombogenicity of the modified films was evaluated by in vitro coagulation time tests, including activated partial thromboplastin time (APTT), prothrombin time (PT), and thrombin time (TT). In the measurement, the samples (1 cm²) were attached to a silcaned tube (diameter: 3 cm; height: 2 mm) and incubated with fresh human platelet-poor-plasma (PPP) for 3 min at 37 °C. The reagents for each coagulation time test were added to the tube, respectively. The clotting time of the plasma solution was measured by a coagulometer (Clot 1A, Innova Co, Ita.). The experiment was repeated in quadruplicate and a mean value was calculated.

III. RESULTS AND DISCUSSION

A. Surface spectroscopic and morphological analysis

The Raman spectrum of the untreated PET film exhibits the characteristic sharp peaks at 1292, 1616, and 1727 cm⁻¹ [Fig. 2(a)]. The peak at 1292 cm⁻¹ is attributed to the ring and the C==O stretch, whereas the 1616 and 1727 cm⁻¹ peaks are due to C==C ring and carbonyl stretch, respectively. The Raman spectrum of the PIII-treated PET reveals a strong carbon layer band on which the PET Raman bands is superimposed [Fig. 2(b)]. The Raman spectrum of carbon film deposited on the Si wafer shows two broad peaks at 1300–1450 cm⁻¹ and 1500–1650 cm⁻¹ as shown in Fig. 2(c). Such a spectrum with an asymmetric broad peak is often seen in a carbon deposit that is called amorphous polymeric-like carbon (PLC) film.¹⁷

Figure 3 shows the ATR-FTIR spectra of the original PET served as a control and PIII-PET. The creation of alkyne end groups (R—C≡C—H) is evidenced by the appearance of a band at 3300 cm⁻¹, which is assigned to C==H stretching vibration mode of the alkyne end group. Large peaks are seen at 1630 cm⁻¹ due to C==C (sp² bonding) of fatty hydrocarbons. The intensity of the peaks assigned to sp³ CH₂ and sp³ CH₃ at around 2850–2950 cm⁻¹ is increased. The result reveals that this surface coating is mostly comprised of a mixture of sp², sp³, and a few sp¹ coordinated carbon atoms in a disordered network.

Figure 4 depicts the XPS survey scan spectra of [Fig. 4(a)] PET and [Fig. 4(b)] PIII-PET surfaces. The chemical composition calculated from the XPS survey scan spectra is shown in Table I. The carbon content of PET surface increases from 75.0% to 85.0% by C₂H₂ PIII treating. In Fig. 5(a), the XPS spectrum for C 1s is resolved into three peaks which represent the interatomic bonds of carbon: C==C (sp³), C==C (sp²), and C==O peak. The dominant features in the spectrum acquired from the treated PET film are sp² (284.5 eV) and C==H bonding (285 ± 0.2 eV). The spectrum is analyzed in more details by fitting Gaussian functions for the proportions of sp³, sp², and C==O as shown in Fig. 5(b). The ratio of sp³ C==C to sp² C==C is 0.25. This indicates that the PLC layer is dominantly graphite carbon.

Figures 6(a) and 6(b) contrast the 5 X 5 µm² surface topography as measured by AFM without any filtering. The surface of the untreated PET sample exhibits a rectangular structure. Pinnaclelike structure can be observed in the image of PIII-treated PET. Each AFM image is analyzed in terms of surface average roughness. The average roughness (Rₐ) of the PET surface modified by acetylene PIII-D decreases from 58.9 nm to 11.4 nm. This result indicates that the surface

![Image](https://via.placeholder.com/150)

**Fig. 7.** Quantity of platelets adhered on the surface of the PET control and PIII-PET.

![Image](https://via.placeholder.com/150)

**Fig. 8.** Morphology of adherent platelets on (a) PET control and (b) PIII-PET after 120 min of incubation in PRP observed by SEM.
morphology of the PET film is significantly affected by C$_2$H$_2$ PIII-D and a carbon layer is deposited on the PET film.

### B. Surface energy and wettability

The total solid surface free energy and its components are determined using double-distilled water and diiodomethane as testing liquids. This determination is based on Young’s equation\(^\text{18}\) that relates the surface tension of a liquid in equilibrium with its vapor. Surface energies together with the contact angle of water and diiodomethane are listed in Table II. After C$_2$H$_2$ PIII-D, the polar component $\gamma_p$ of surface energy increases from 2.4 mN/m to 12.3 mN/m and $\gamma_p/\gamma_d$ increases from 0.06 to 0.35. The wettability of the PET with the PLC coating is improved by C$_2$H$_2$ PIII-D.

### C. Platelet adhesion and activation

Platelet adhesion and activation is an indicator of the antithrombogenicity of surface modified PET films. The platelet adhesion test shows significant difference in the behavior of platelet adhesion among different PET surfaces. Figure 7 displays the numbers of adherent platelets on the surface of the PET control and PIII-PET after 20 min incubation. The number of adherent platelets on PIII-PET is lower than that on the untreated surface. On the PIII-PET sample, an average of 60 contact-adherent platelets are present, compared to 120 contact-adherent platelets present on the PET control. This suggests that adhesion of platelets is significantly suppressed by the amorphous carbon film deposited on PET.

SEM is used to study the morphology of adhered platelets and to compare the platelets shape changes on the different surfaces after 120 min incubation. As shown in Fig. 8(b), the adherent platelets on the surface of PIII-PET are relatively isolated and round. In comparison, most of the adherent platelets on the PET control are in aggregation and spreading pseudopodium [Fig. 8(b)].

It is believed that the initial adsorption of protein from blood onto a material surface has a great influence on platelet adhesion and activation.\(^\text{19}\) Therefore, a good understanding of the relationships between the material surface and plasma proteins (fibrinogen, g-globulin, and albumin) is very important for surface design of biomedical materials. For interfacial tension ($\gamma_{ij}$) between condensed phase $i$ and $j$, a relative evaluation can be made:

\[
\gamma_{ij} = (\alpha_i - \alpha_j)^2 + (\beta_i - \beta_j)^2 + \Delta_{ij},
\]

where $\alpha_S$ and $\beta_S$ defined by Kaelble and Moacanin\(^\text{20}\) are dispersion $\alpha_S = (\gamma_S^0)^{1/2}$ and polar $\beta_S = (\gamma_S^1)^{1/2}$ components of polymer surface, respectively. In this work, interfaces dominated by van der Waals interactions and the term $\Delta_{ij}$ describe the ion–covalent interaction that can be considered negligible. According to Ref. 21, $\alpha_i$ and $\beta_i$ of plasma proteins are listed in Table III. The interfacial energy parameters for different proteins can be calculated as given in Table III for PET surface ($\gamma_p = 6.4$ dyn/cm$^{1/2}$, $\gamma_d = 1.6$ dyn/cm$^{1/2}$), and an amorphous carbon film deposited by C$_2$H$_2$ PIII on PET (2) $\alpha_i = 6.9$ (dyn/cm$^{1/2}$), and $\beta_i = 3.5$ (dyn/cm$^{1/2}$). It is expected that the conformation of adsorbed plasma protein will change. Several studies\(^\text{22,23}\) have indicated that this conformational change plays an important role in platelet adhesion and activation. Our previous results\(^\text{24}\) suggest that the higher the interfacial energy, the larger the conformation changes. From Table III, it appears that the interfacial energy is lowest with albumin in both surfaces compared to fibrinogen and g-globulin. However, both the interfacial energy with albumin and fibrinogen or g-globulin in the case of PIII-PET surface is lower than those on the untreated PET surface. Hence, the possibility of weak adsorption and less conformation of these proteins is suggested on the PLC films.

As the evaluation criteria of the abnormality of blood plasma in clinical tests, the APTT, PT, and TT have recently been used in the evaluation of the \textit{in vitro} antithrombogenicity of biomaterials.\(^\text{25,26}\) Table IV shows the APTT, PT, and TT of the PPP in contact with the test materials. In this test, glass and silanized glass are used as positive and negative controls, respectively. PT and APTT are generally used to detect the degree of activation of the exogenic and endogenic clotting system.\(^\text{27}\) TT represents the duration from the addition of thrombin to the formation of the insoluble fibrin.

The PT of PPP incubated with various materials is not altered much, whereas the APTT and TT values of the PPP in

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**Table III.** Intercal energy parameters of PET and PIII-PET with plasma protein system.

<table>
<thead>
<tr>
<th>Protein</th>
<th>Polar/nonpolar ratio</th>
<th>$\alpha_i$ (dyn/cm$^{1/2}$)</th>
<th>$\beta_i$ (dyn/cm$^{1/2}$)</th>
<th>PET surface $\gamma_{ij}$ (dyn/cm)</th>
<th>PIII-PET surface $\gamma_{ij}$ (dyn/cm)</th>
<th>$\frac{\gamma_{ij} - \beta_i^2 - \beta_i}{\alpha_i - \alpha_i}$</th>
<th>$\frac{\gamma_{ij} - \beta_i}{\alpha_i}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fibrinogen</td>
<td>1.626</td>
<td>4.972</td>
<td>6.346</td>
<td>25.0</td>
<td>11.4</td>
<td>11.6</td>
<td>2.2</td>
</tr>
<tr>
<td>g-globulin</td>
<td>1.205</td>
<td>5.428</td>
<td>9.661</td>
<td>20.4</td>
<td>20.8</td>
<td>8.1</td>
<td>2.9</td>
</tr>
<tr>
<td>Albumin</td>
<td>1.072</td>
<td>5.602</td>
<td>5.789</td>
<td>18.8</td>
<td>22.8</td>
<td>6.8</td>
<td>3.3</td>
</tr>
</tbody>
</table>

\(^a\)For values of $\alpha_i = 6.4$ (dyn/cm$^{1/2}$) and $\beta_i = 1.6$ (dyn/cm$^{1/2}$).

\(^b\)For values of $\alpha_i = 6.9$ (dyn/cm$^{1/2}$) and $\beta_i = 3.5$ (dyn/cm$^{1/2}$).

**Table IV.** \textit{In vitro} coagulation time (APTT, PT, and TT) of PPP incubated with various materials.

<table>
<thead>
<tr>
<th>Samples</th>
<th>APTT (s)</th>
<th>PT (s)</th>
<th>TT (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPP + glass</td>
<td>50.7 ± 2.0</td>
<td>13.2 ± 0.4</td>
<td>17.4 ± 0.8</td>
</tr>
<tr>
<td>PPP + silanized glass</td>
<td>57.4 ± 0.9</td>
<td>13.9 ± 0.3</td>
<td>20.6 ± 1.1</td>
</tr>
<tr>
<td>PPP + PIII-PET</td>
<td>51.4 ± 1.1</td>
<td>13.1 ± 0.2</td>
<td>18.6 ± 0.7</td>
</tr>
<tr>
<td>PPP + II-PET</td>
<td>56.4 ± 1.2</td>
<td>13.4 ± 0.2</td>
<td>21.2 ± 0.3</td>
</tr>
</tbody>
</table>

contact with the PIII-PET surface are longer than those of the untreated PET as well as positive and negative controls. Hence, the antithrombogenic effect of the amorphous PLC film deposited on PET is to interdict the endogenic conformation of thrombin.

According to the aforementioned discussion, the suppression of the platelet adhesion and activation on the amorphous PLC film deposited by C\textsubscript{2}H\textsubscript{2} PIII-D depends not only on the presence of adsorbed plasma proteins but also on the conformation change of adsorbed plasma proteins. Another plausible reason for good blood compatibility of the amorphous PLC film is that this surface can interdict the contact activation path of the clotting process.

IV. CONCLUSION

Amorphous PLC coatings are fabricated on PET films by acetylene PIII-D and characterized by Raman, XPS, ATR-FTIR, and AFM. Platelet adhesion and activation are suppressed on the PLC coatings compared with the untreated PET film. Our results suggest that one reason for the good hemocompatibility is that the PLC coating minimizes its interactions with plasma protein and slightly changes the conformation of adsorbed plasma protein. The other reason is that this coating suppresses the endogenic clotting system of blood.

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